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QUANTITIES OF BISPHENOL A LEACHED FROM PLASTIC WASTE SAMPLES

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ABSTRACT

To quantify the leaching of bisphenol A into water, various samples of plastic waste were cut into small pieces, soaked in water for two weeks at room temperature in the dark, and the concentration of bisphenol A in the water determined by gas chromatography / mass spectrometry (GC/MS). The amount of bisphenol A leached from the plastic wastes ranged from undetectable to 139 $\mu\text{g/g}$. The detection limit was 2 ng/g when 100 g of plastic waste was used. Polyvinyl chloride products yielded the highest concentrations because bisphenol A is used in its manufacture as a stabilizer. ©1999 Elsevier Science Ltd. All rights reserved

Keywords

Bisphenol A, Plastic waste, Leaching, GC/MS.

INTRODUCTION

Bisphenol A, 4,4'-(1-methylethylidene)bisphenol, is used in the manufacture of polycarbonate and epoxy- and phenoxy- resins. It is also used as stabilizing material or antioxidant for many types of plastics such as polyvinyl chloride [1]. The production and use of bisphenol A is increasing as the use of such plastics increases. In Japan, the production of bisphenol A was about 250 000 tons in 1996 [2]. Bisphenol A has weak acute toxicity to aquatic organisms; LC_{50} or EC_{50} levels for fish and invertebrates range from 1.1 mg/L to 10 mg/L [3, 4]. Recently, it was revealed that bisphenol A which leached from a polycarbonate flask during autoclaving had estrogenic activity [5]. It has also been shown that bisphenol A leached from lacquer coated cans [6] and baby feeding-bottles [7]. In these studies, bisphenol A was present due to the hydrolysis of the polymer caused by thermal treatment. Bisphenol A was also found in saliva collected from patients who were treated with a bisphenol A diglycidyl ether (BADGE) based dental sealant [8]. In this case, unreacted BADGE in the sealant was leached from the site of application and underwent hydrolysis to give bisphenol A. Kamiura et. al. reported that bisphenol A occurred in the atmosphere of Japan at levels ranging from 2.9 to 3.6 ng/m^3 [9]. They suggested that bisphenol A in the air was released by the combustion of polycarbonate or

epoxy products. In our previous study of the organic components of hazardous waste landfill leachates, we found bisphenol A at high concentrations and high frequency [10]. The concentration of bisphenol A in the most polluted leachate was 12.3 $\mu\text{g/L}$. Though this level is lower than reported toxic concentrations for invertebrates or fish, leaching of bisphenol A is likely to become a significant problem because of the large production and wide use of this compound. Moreover, the report of the estrogenic behavior of bisphenol A [5] suggests that it may serve as an endocrine disrupter at environmental concentrations well below acutely toxic levels. Bisphenol A in landfill leachates may originate in the reclamation of waste plastics, but there is currently no clear information to identify the relevant plastics or explain the leaching mechanism.

The aim of this study was to quantify the leaching of bisphenol A from waste plastics and thereby clarify the mechanism for its environmental occurrence. Concentrations of bisphenol A in plastic waste samples and in experimentally-generated leachates were determined by gas chromatography / mass spectrometry (GC/MS). The relationship between the type of waste plastic material and the quantity of bisphenol A leaching into water was investigated.

EXPERIMENTAL

Reagents and Materials. All solvents and reagents were of pesticide analysis grade and were purchased from Wako Pure Chemicals Industry Ltd.(Japan). Bisphenol A was purchased from Wako Pure Chemicals Industry Ltd.. Water was distilled and then purified by a Milli-Q Water Purification System (Waters, US). The waste plastic samples used in this study are listed in Table 1. They were collected at a disposal landfill site in April 1996 in Japan.

GC/MS Apparatus and Operating conditions. For qualitative and quantitative analyses, an HP model 5890 II plus gas chromatograph equipped with an HP model 5972 mass spectrometer was used (Hewlett-Packard, US). The injection temperature was 260 °C and the injection mode was splitless. The carrier gas was helium and the flow rate was 1 mL/min. A PTE-5 capillary column (30 m \times 0.25 mm i.d., 0.25 μm d_f) was used (Supelco, US). The oven temperature was initially 60 °C, and was raised to 260 °C at a rate of 10 °C/min, then held at that temperature for 5 min. The MS transfer line temperature was 280 °C. For qualitative analysis, the MS was operated in scan mode. The scan range was from m/z 10 to 500 and the scan cycle was 1.4 scan/s. For quantitative analysis, the MS was operated in the selected ion monitoring (SIM) mode. Monitored ions were m/z 213.1 and 228.1. The dwell time was 50 ms.

Determination of Bisphenol A in Waste Plastic Samples. About one gram of each waste plastic material was cut into small pieces, placed in a 200 mL Erlenmeyer flask, and dissolved in 20 mL of chloroform. Then 50 mL of methanol was slowly added to the solution to precipitate the dissolved polymer. The solution was allowed to settle for a few hours to precipitate the polymer completely. One μL of supernatant was sampled with a microsyringe and injected into the GC/MS to determine the bisphenol A.

Table 1. Plastic waste samples used in this study.

| No. | Sample | Weight (g) | Period (days) | No. | Sample | Weight (g) | Period (days) |
|-----|--|---------------|------------------|-----|-------------------------------------|---------------|------------------|
| 1 | Polycarbonate, Food stock box, transparent | 102.7 | 12 | 10 | Sheet, translucent | 47.1 | 14 |
| 2 | Film, black | 52.9 | 14 | 11 | Film, translucent | 20.2 | 13 |
| 3 | Electrical plug, gray | 136.1 | 14 | 12 | Electrical plug, black | 71.8 | 13 |
| 4 | Polyvinyl chloride, electrical cord, gray | 106.0 | 14 | 13 | Synthetic leather, gray | 25.9 | 14 |
| 5 | Sheet, white | 28.6 | 13 | 14 | Electrical plug, green | 123.1 | 14 |
| 6 | Electrical plug, white | 73.0 | 13 | 15 | Phenol resin, printed circuit board | 45.6 | 14 |
| 7 | Synthetic leather, gray | 68.8 | 13 | 16 | Polycarbonate, compact disk | 80.6 | 14 |
| 8 | Electrical plug, blue | 128.4 | 14 | 17 | Polyvinyl chloride, pipe, gray | 81.1 | 14 |
| 9 | Wool like fiber, gray | 8.9 | 14 | | | | |

Procedure for the Bisphenol A Leaching Experiment. Each waste plastic material was cut into small pieces and transferred to a 500 mL glass beaker. The beaker was filled with 300 mL of water and covered with aluminum foil. The sample was left in dark at room temperature for about 2 weeks.

Sample Preparation for the Determination of Bisphenol A. The leachate water, formed as described above, was filtered through glass wool and 30 g of sodium chloride dissolved in the filtrate. The filtered leachate sample was then acidified with hydrochloric acid ($\text{pH} < 2$) and transferred to a separatory flask. The solution was extracted twice with 50 mL of dichloromethane by shaking for 5 min. The bulked extract was dried by passage through a short column plugged with anhydrous sodium sulfate and was then concentrated on a rotary evaporator to about 2 mL. The extract was further concentrated to 1 mL under a nitrogen stream. One μL of the concentrated sample was injected into the GC/MS and analyzed.

RESULTS AND DISCUSSION

Analysis of Bisphenol A Leached from Plastic Wastes. HPLC, GC and GC/MS [11] are commonly used to determine bisphenol A. Many kinds of plastic additives, such as phthalates, with the potential to interfere in the determination of bisphenol A may leach from the plastic to the water. To avoid such interference, a GC/MS method was adopted because of its high selectivity and sensitivity. Therefore, no clean-up procedure

Table 2. Levels of bisphenol A leached from plastic wastes.

| No. | Concentration of Bisphenol A ($\mu\text{g/L}$)* | Concentration normalized to plastic weight (ng/g) |
|-----|--|--|
| 1 | 1.3 | 4.2 |
| 2 | 1.6 | 9.1 |
| 3 | 1.4 | 3.3 |
| 4 | 700 | 1 980 |
| 5 | N.D. | N.D. |
| 6 | N.D. | N.D. |
| 7 | 2 250 | 9 810 |
| 8 | N.D. | N.D. |
| 9 | N.D. | N.D. |
| 10 | 2.6 | 16.8 |
| 11 | N.D. | N.D. |
| 12 | 1.8 | 7.7 |
| 13 | 12 300 | 139 000 |
| 14 | N.D. | N.D. |
| 15 | 10.1 | 67.7 |
| 16 | 6.0 | 23.3 |
| 17 | 3.0 | 10.7 |

* Detection limit is 0.58 $\mu\text{g/L}$.

was needed. The leachate sample was acidified to enhance the extraction efficiency in each case. Recovery rates of bisphenol A from water were from 73 to 120 % for a concentration range of 0.4 to 2 $\mu\text{g/L}$. The method detection limit was 0.58 $\mu\text{g/L}$ based on 3σ of the blank response. When 100 g of waste plastic was used for the leaching experiment described above, the detection limit normalized to the weight of plastic weight became approximately 2 ng/g.

Levels of Bisphenol A Leached from Plastic Wastes. The levels of bisphenol A leached from waste plastics are listed in Table 2. Because of a lack of information on the composition of the waste plastics, it is difficult to assess the relationship between their composition and the amount of bisphenol A leached from them. A soft polyvinyl chloride product, such as the insulation on electrical wire (sample 4), gave a high concentration of bisphenol A; 1.98 $\mu\text{g/g}$. The SIM chromatogram of the leached extract of this sample is presented in Figure 1. The bisphenol A that leached from this sample was probably used as a stabilizer for the polyvinyl chloride.

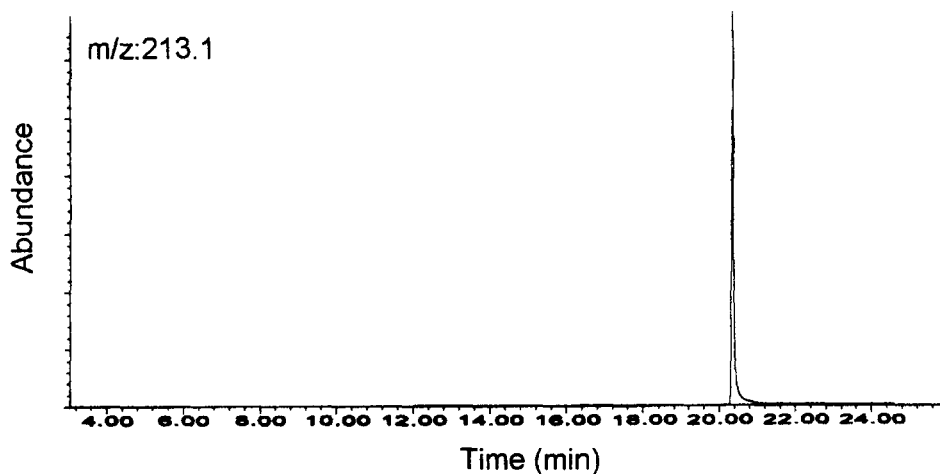


Figure 1. SIM Chromatogram of leachate of plastic waste sample 4.

On the other hand, a hard polyvinyl chloride product (sample 17) gave a relatively low concentration. Several waste plastics gave, such as the synthetic leather (samples 7 and 13) yielded high concentrations of bisphenol A. The concentrations of bisphenol A that leached from sample 7 and 13 were 9.8 and 139 $\mu\text{g/g}$, respectively. For sample 13, about 26 g of plastic waste were soaked in 300 mL of water. Thus the final concentration of bisphenol A in the leachate was 12 mg/L. This concentration exceeded the LC_{50} or EC_{50} values that have been reported for aquatic organisms [3, 4]. In the qualitative analysis of the leachate samples, the total ion chromatogram of the leachate extract from sample 13 was very similar to that of sample 4 (Figure 2a,b). Beilstein tests (which demonstrate the presence of halogen atoms in plastics) were positive for these synthetic leathers. So it is reasonable to assume that these synthetic leathers contained polyvinyl chloride and that the bisphenol A used as a stabilizer in the polyvinyl chloride leached out. The food stock box (sample 1) and the compact disk (sample 16), both polycarbonate products, yielded low concentrations of bisphenol A; 4.2 and 23.3 ng/g, respectively. There are two possible origins for the bisphenol A leaching from a polycarbonate product; migration of residual bisphenol A and hydrolysis of the polycarbonate itself. Biles et. al. reported that the concentration of bisphenol A in water stored in a polycarbonate carboy for 39 weeks was 4.7 ng/L. This value is small because under normal conditions (room temperature and neutral pH) the hydrolysis of polycarbonate is negligible. Thus, only the small amount of residual bisphenol A leached from the polycarbonate product to water and the low level of bisphenol A did not increase.

The concentrations of bisphenol A in waste plastics are shown in Table 3. The concentrations of bisphenol A in polycarbonate products were as large as those in polyvinyl chloride products. Waste plastics were classified into three groups according to the relationship between their concentration of bisphenol A and the amount of bisphenol A leaching from them; (1) high bisphenol A content and high degree of leaching, (2) high bisphenol

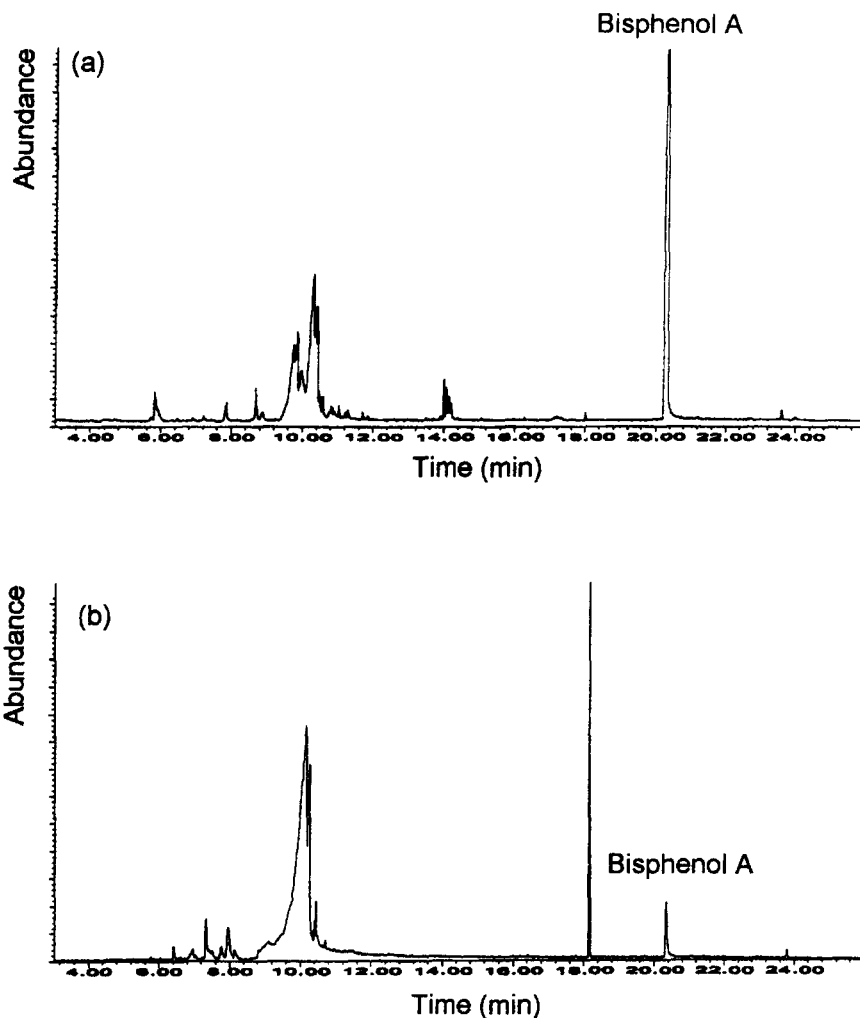


Figure 2. Total ion chromatograms of leachates. (a) Sample 13. (b) Sample 4.

A content and low degree of leaching, and (3) low bisphenol A content and low degree of leaching (Figure 3). Samples 4, 7 and 13 were included in the first group. The several percent of bisphenol A contained in these waste plastics leached to the water. Polycarbonate products belonged to the second group. Only a very low percentage (10^{-3}) of the bisphenol A content leached from them. Therefore, in evaluating the environmental impact of bisphenol A in waste plastics, the first group are more significant than the second and third groups plastics because of its high leaching rates.

Yasuhara et. al. reported that bisphenol A was found in leachate samples from hazardous waste disposal sites in Japan [10]. Bisphenol A was found at five sites out of the eight that were sampled. Levels ranged from 0.15

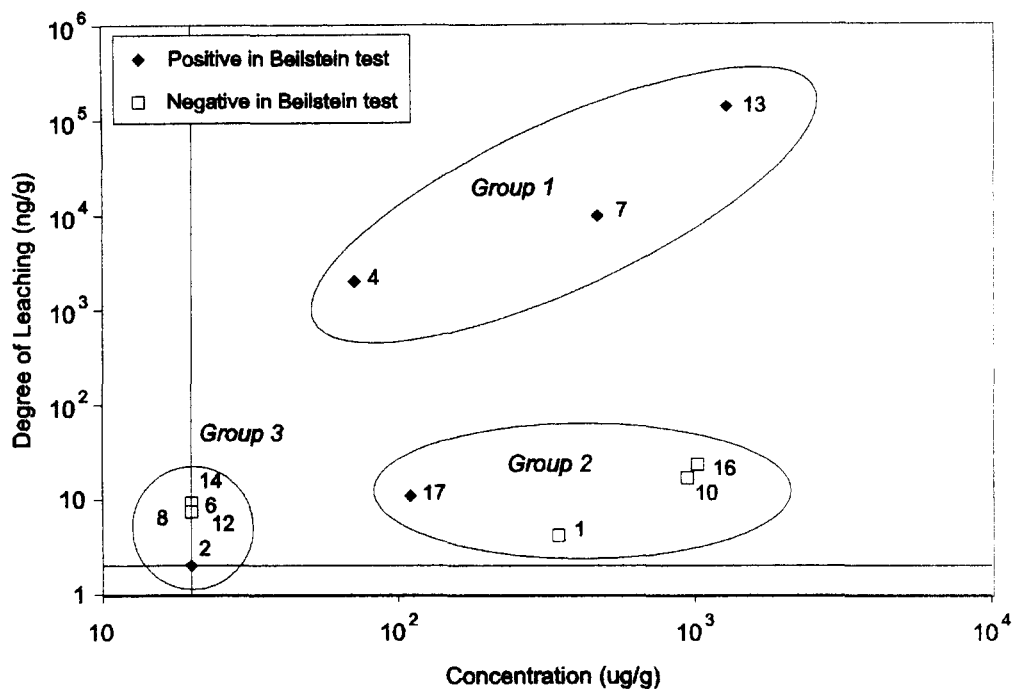


Figure 3. Relation between the concentration of bisphenol A in the plastic wastes and the degree of leaching.

Table 3. Bisphenol A concentrations in plastic wastes.

| No. | Bisphenol A ($\mu\text{g/g}$)* | Percentage of bisphenol A leached from sample |
|-----|----------------------------------|---|
| 1 | 347 | 1.1×10^{-3} |
| 4 | 71 | 2.9 |
| 6 | N.D. | — |
| 7 | 467 | 2.1 |
| 8 | N.D. | — |
| 10 | 942 | 1.8×10^{-3} |
| 13 | 1 280 | 11 |
| 14 | N.D. | — |
| 16 | 1 020 | 2.3×10^{-3} |
| 17 | 110 | 9.7×10^{-3} |

* Detection Limit is 20 $\mu\text{g/g}$.

to 12.3 µg/L. Although the high frequency of finding bisphenol A and the high concentrations of this compounds have not been fully explained yet, bisphenol A found in landfill leachates may originate in reclaimed waste plastics. As mentioned above, waste plastics belonging to the group with high leaching rates, such as polyvinyl chloride may be one of the most important source of bisphenol A found in landfill leachate samples. Moreover, since the production and use of polyvinyl chloride products are far larger than ones of polycarbonate or epoxy-resin products, more attention should be paid to the use of bisphenol A as stabilizer for polyvinyl chloride and the possible environmental consequences of this use.

References

1. M. Ash, I. Ash, *Handbook of Plastic and Rubber Additives*, Gower, Hampshire, UK (1995)
2. Ministry of International Trade and Industry of Japan, *Kagaku Kougyo Toukei Nempo*, Tsusho -Sangyo Chosa-Kai, Tokyo, JAPAN (in Japanese) (1997)
3. H. C. Alexander, D. C. Dill, L. A. Smith, P. A. Guiney, P. B. Dorn, Bisphenol A: acute aquatic toxicity, *Environ. Toxicol. Chem.*, **7**, 19-26 (1998)
4. P. B. Dorn, C. S. Chou, J. J. Gentempo, Degradation of bisphenol A in natural waters, *Chemosphere*, **16**, 1501-1507 (1987)
5. A. V. Krishnan, P. S. Starhis, F. Permuth, L. Tokes, D. Feldman, Bisphenol-A: an estrogenic substance is released from polycarbonate flasks during autoclaving, *Endocrinology*, **132**, 2279-2286 (1993)
6. J. A. Brotons, M. F. Olea-Serrano, M. Villalobos, V. Pedraza, N. Olea, Xenoestrogens released from lacquer coatings in food cans, *Environ. Health Perspect.*, **103**, 608-612 (1995)
7. J.E. Biles, T. P. McNeal, T. H. Begley, H. C. Hollifield, Determination of bisphenol A in reusable polycarbonate food-contact plastics and migration to food-simulating liquids, *J. Agric. Food Chem.*, **45**, 3541-3544 (1997)
8. N. Olea, R. Pulgar, P. Perez, F. Olea-Serrano, A. Rivas, A. Novillo-Tertrell, V. Pedraza, A. M. Soto, C. Sonnenschein, Estrogenicity of resin-based composites and sealants used in dentistry, *Environ. Health Perspect.*, **104**, 298-305 (1996)
9. T. Kamiura, Y. Tajima, T. Nakahara, Determination of bisphenol A in air, *J. Environ. Chem.*, **7**, 275-279 (in Japanese) (1997)
10. A. Yasuhara, H. Shiraishi, M. Nishikawa, T. Yamamoto, T. Uehiro, O. Nakasugi, T. Okumura, K. Kenmotsu, H. Fukui, M. Nagase, Y. Ono, Y. Kawagoshi, K. Baba, Y. Noma, Determination of organic components in leachates from hazardous waste disposal sites in Japan by gas chromatography/mass spectrometry, *J. Chromatogr. A*, **774**, 321-332 (1997)
11. M. del Olmo, A. González-Casado, N. A. Navas, J. L. Vilchez, Determination of bisphenol A (BPA) in water by gas chromatography-mass spectrometry, *Anal. Chim. Acta*, **346**, 87-92 (1997)